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(21) International Application Number: PCT/NL99/00350 (22) International Filing Date: 4 June 1999 (04.06.99) (30) Priority Data: 98201944.0 10 June 1998 (10.06.98) EP (71) Applicant (for all designated States except US): COÖPERATIEVE VERKOOP- EN PRODUCTIEV- ERENIGING VAN AARDAPPELMEEL EN DERIVATEN AVEBE B.A. [NL/NL]; Beneden Oosterdiep 27, NL-9641 JA Veendam (NL). (72) Inventor; and (75) Inventor/Applicant (for US only): KESSELMANS, Ronald, Peter, Wilhelmus [NL/NL]; Kromkampen 11, NL-9468 HK Annen (NL). (74) Agent: OTTEVANGERS, S., U.; Vereenigde Octrooibureaux, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PHOSPHATE ESTERS OF STARCH		
(57) Abstract		
<p>The invention relates to a process for preparing a phosphate ester of starch, wherein a starch comprising at least 95 wt.%, based on dry substance of the starch, of amylopectin, is reacted with phosphoric acid or an orthophosphate salt at a temperature of 75-250 °C under semi-dry conditions.</p>		

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Title: Phosphate esters of starch

The invention relates to a process of preparing a phosphate ester of starch, a phosphate ester of starch obtainable by said process, as well as the use of said phosphate ester, particularly in the paper industry.

5 The development of phosphate esters of starch for the paper industry dates back to the early sixties. These products are mostly applied in paper coatings and confer unique properties to the coatings.

10 As a co-binder in paper coatings, phosphate esters show a reduced mottling tendency and a good ink receptivity. Further, the esters have a high binding power and show a good water retention. Also, the viscosity stability and dispersibility are quite good.

15 Conventionally, phosphate esters of starch are prepared by reaction of starch with phosphoric acid or sodium orthophosphate at about 100-150°C under low moisture conditions (<5 wt.% of water). To obtain a product having a relatively low viscosity, in addition to the phosphoric acid, another inorganic acid, such as sulfuric acid, may be
20 present. In this reaction, urea is used as a catalyst. It is present during the reaction in an amount of 10-25 wt.%, based on the starch. The use of urea results in a faster reaction with a lower resulting free-phosphate content and less yellowing of the final product. Further, the presence of urea
25 results in the formation of carbamate groups in the starch. Due to this reaction of urea with starch, approximately 10-20 wt.% of the nitrogen present in the reaction mixture is liberated in the form of ammonia, causing a significant environmental problem.

30 The present invention aims to provide an improved process for preparing a phosphate ester of starch, wherein the environmental problem of emission of ammonia is reduced. It is further an object of the invention to provide a process wherein a phosphate ester is prepared, which has highly
35 advantageous properties. In other words, the reduction of

ammonia emission may not negatively affect the properties of the phosphate ester that is prepared.

Surprisingly, it has now been found that the use of a specific type of starch for preparing the desired phosphate ester leads to a reduction of the amount of required urea during the reaction, while at the same time a phosphate ester is obtained having highly favorable characteristics.

Accordingly, the invention relates to a process for preparing a phosphate ester of starch, wherein a starch comprising at least 95 wt.%, based on dry substance of the starch, of amylopectin, is reacted with phosphoric acid or an orthophosphate salt at a temperature of 100-175°C under low moisture conditions (<5 wt.% of water).

It is a great advantage of a process according to the invention that significantly less urea is necessary to prepare a phosphate ester of starch having properties which

are at least as favorable, when compared with the known processes. It has even proven possible to perform the process without using urea. This not only leads to an economically more attractive process, but, importantly, leads to a significantly smaller amount of ammonia produced during the reaction. Furthermore, it has been found that the present process requires less energy and can be effected in less time than the preparation processes of conventional phosphate esters of starch. Consequently, the present process is substantially less harmful to the environment.

As has been set forth above, in accordance with the invention, a phosphate ester is prepared from a starch which has a very high amylopectin content. Most starch types consist of granules in which two types of glucose polymers are present. These are amylose (15-35 wt.% on dry substance) and amylopectin (65-85 wt.% on dry substance). Amylose consists of unbranched or slightly branched molecules having an average degree of polymerization of 1000 to 5000, depending on the starch type. Amylopectin consists of very large, highly branched molecules having an average degree of

polymerization of 1,000,000 or more. The commercially most important starch types (maize starch, potato starch, wheat starch and tapioca starch) contain 15 to 30 wt.% amylose.

Of some cereal types, such as barley, maize, millet, wheat, milo, rice and sorghum, there are varieties of which the starch granules nearly completely consist of amylopectin. Calculated as weight percent on dry substance, these starch granules contain more than 95%, and usually more than 98% amylopectin. The amylose content of these cereal starch granules is thus less than 5%, and usually less than 2%. The above cereal varieties are also referred to as waxy cereal grains, and the amylopectin-starch granules isolated therefrom as waxy cereal starches.

In contrast to the situation of cereals, root and tuber varieties of which the starch granules nearly exclusively consist of amylopectin are not known in nature. For instance, potato starch granules isolated from potato tubers usually contain about 20% amylose and 80% amylopectin (wt.% on dry substance). During the past 10 years, however, successful efforts have been made to cultivate by genetic modification potato plants which, in the potato tubers, form starch granules consisting for more than 95 wt.% (on dry substance) of amylopectin. It has even been found feasible to produce potato tubers comprising substantially only amylopectin.

In the formation of starch granules, various enzymes are catalytically active. Of these enzymes, the granule-bound starch synthase (GBSS) is involved in the formation of amylose. The presence of the GBSS enzyme depends on the activity of genes encoding for said GBSS enzyme. Elimination or inhibition of the expression of these specific genes results in the production of the GBSS enzyme being prevented or limited. The elimination of these genes can be realized by genetic modification of potato plant material or by recessive mutation. An example thereof is the amylose-free mutant of the potato (amf) of which the starch substantially only

contains amylopectin through a recessive mutation in the GBSS gene. This mutation technique is described in, inter alia, J.H.M. Hovenkamp-Hermelink et al., "Isolation of amylose-free starch mutant of the potato (*Solanum tuberosum* L.)", Theor.

- 5 Appl. Gent., (1987), 75:217-221, and E. Jacobsen et al., "Introduction of an amylose-free (amf) mutant into breeding of cultivated potato, *Solanum tuberosum* L., Euphytica, (1991), 53:247-253.

- 10 Elimination or inhibition of the expression of the GBSS gene in the potato is also possible by using so-called antisense inhibition. This genetic modification of the potato is described in R.G.F. Visser et al., "Inhibition of the expression of the gene for granule-bound starch synthase in potato by antisense constructs", Mol. Gen. Genet., 1991),
15 225:289-296.

By using genetic modification, it has been found possible to cultivate and breed roots or tubers, for instance potatoes, yam, and cassave (Patent South Africa 97/4383), of which the starch granules contain little or no amylose. As
20 referred to herein, by amylopectin starch is intended the starch granules isolated from a natural source having an amylopectin content of at least 95 wt.% based on dry substance.

- Regarding production possibilities and properties,
25 there are significant differences between amylopectin-potato starch on the one hand, and the waxy cereal starches on the other hand. This particularly applies to waxy maize starch, which is commercially by far the most important waxy cereal starch. The cultivation of waxy maize, suitable for the
30 production of waxy maize starch is not commercially feasible in countries having a cold or temperate climate, such as The Netherlands, Belgium, England, Germany, Poland, Sweden and Denmark. The climate in these countries, however, is suitable for the cultivation of potatoes. Tapioca starch, obtained
35 from cassave, may be produced in countries having a warm

climate such as is found in regions of South East Asia and South America.

The composition and properties of root and tuber starches, such as amylopectin-potato starch and tapioca amylopectin-starch differ from those of the waxy cereal starches. Amylopectin-potato starch has a much lower content of lipids and proteins than the waxy cereal starches. Problems regarding odor and foaming, which, because of the lipids and/or proteins, may occur when using waxy cereal starch products (native and modified), do not occur or occur to a much lesser degree when using corresponding amylopectin-potato starch products.

The invention contemplates the preparation of phosphate esters from cereal and fruit starches on the one hand, and root and tuber starches on the other hand. Of the cereal starches, waxy maize starch has proven suitable. In general, however, root and tuber starches are more preferred. As has been indicated above, it is advantageous to use a starch having a very low content of lipids and/or proteins. The presence of lipids and/or proteins increases the risk of undesired side reactions taking place, such as Maillard reactions. The desire to avoid these reactions puts a limitation on the reaction conditions possible during the present preparation process. In addition, it has been found that lipids present in the starch may form complexes with the phosphate esters that are formed in a process according to the invention. Dependent on the application of the phosphate esters, these complexes may lead to less advantageous results. The use of amylopectin-potato starch and amylopectin-tapioca starch has been found to lead to a particularly stable, light colored phosphate ester.

Suitable derivatives of a starch comprising at least 95 wt.%, based on dry substance of the starch, of amylopectin may be prepared via etherification, esterification, or degradation reactions, or combinations thereof. Preferably, a starch derivative obtained by etherification is used. For a

general description of these modification reactions of starch reference is made to "Modified Starches: Properties and Uses", O.B. Wurzburg, CRC Press Inc., 1987.

5 Etherification of starch may be effected by reaction with a reagent comprising a halogen, halohydrin, epoxide or glycidyl reactive site. The reaction may be performed under (semi-)dry conditions, in suspension (water or organic solvent), or in aqueous solution. Preferably, the reaction is carried out in aqueous suspension. Etherification leads to
10 alkylated, hydroxyalkylated, or hydroxyarylated starches. The alkyl or aryl chain of the substituent may vary from 1 to 20 carbon atoms, preferably from 1 to 12 carbon atoms, more preferably from 1 to 4 carbon atoms. Suitable examples of reagents include methyl chloride, ethylene oxide, propylene
15 oxide, allyl glycidyl ether, propyl glycidyl ether, phenyl glycidyl ether and combinations thereof.

In a special case of etherification, cationic starch derivatives may be prepared. For example, diethylaminoethyl chloride, glycidyltrialkylammonium salts, or 1-chloro-2-
20 hydroxypropyltrialkyl ammonium salts, wherein the alkyl groups may vary from 1 to 20 carbon atoms or wherein one or more alkyl groups are replaced by allyl groups, are used for the preparation of cationic starches. It is also possible to use any combination of alkylated, hydroxyalkylated,
25 hydroxyarylated, or cationically derivatized starches may be employed.

As has been indicated above, in the present process, starch or a derivative thereof is reacted with phosphoric acid or with an orthophosphate salt, preferably with the
30 sodium salt. The amount in which the acid or the salt is added to the starch to be converted to a phosphate ester depends on the desired properties of the product to be prepared and the reaction time available. When phosphoric acid is used, it is also possible to use partially
35 neutralized phosphoric acid. Under the preferred reactions conditions the pH is lower than 7, more preferably lower than

4. Optionally, the phosphate ester may be neutralized by mixing with alkaline salts, such as sodium carbonate.

Preferably, phosphoric acid is employed in an amount ranging from about 0.5 to 10 wt.%, more preferably from 1 to 6 wt.%,

5 based on dry substance of starch. Alternatively, a mixture of orthophosphate salts may be used. Suitable orthophosphate salts are mono-, di- and trialkalimetal salts of phosphate.

These may be used in amounts up to 5 wt.%, based on the starch. Examples include sodium dihydrogen phosphate,

10 disodium hydrogen phosphate, and trisodium phosphate.

Under certain circumstances, another inorganic acid, in addition to the phosphoric acid, may be used. This applies particularly when a phosphate ester of starch is desired, which has a relatively low viscosity. Suitable examples of

15 additional inorganic acids include hydrochloric acid and sulfuric acid. These acids may be used in amounts up to 2.5

wt.%, based on starch.

Further, the present process is preferably carried out in the presence of urea. Urea promotes the reaction rate as well as the yield of the esterification reaction. Urea may

20 suitably be used in amounts up to 25 wt.%, preferably less than 15 wt.%, based on the starch (dry weight). Generally, the amount of urea will be between 0 and 15 wt.%, preferably between 0 and 10 wt.%, even more preferably between 1 and 5

25 wt.%, based on the starch (dry weight).

Preferably, the reaction for preparing a phosphate ester of the starch or the derivative thereof will be carried out in the absence of a solvent, i.e. under semi-dry or substantially dry conditions. These conditions may be

30 achieved by drying the mixture of the starch to be converted and the acid before heating. Preferably, the mixture will be dried to a moisture content of less than 10 wt.%, more preferably to less than 5 wt.%. Drying may be performed by any known drying technique, such as fluid bed, pneumatic or

35 flash drying.

The temperature at which the starch will preferably be converted to a phosphate ester lies between 75 and 250°C, more preferably between 100 and 180°C, even more preferably between 105 and 150°C. The duration of the reaction will
5 generally be less than 1 hour, dependent on the amount of starch to be converted and on the desired viscosity of the phosphate ester to be prepared.

The esterification process may be carried out using any known technology, such as the Noredux process, or the use
10 of a fluid bed reactor, or a rotating vessel. Preferably, the process is carried out in a fluid bed reactor. Particularly when the esterification is performed under substantially dry conditions it is advantageous to use a fluid bed reactor in order to provide an optimal contact between the hot air in
15 the reactor and the starch that is being converted to a phosphate ester.

The invention further relates to a phosphate ester of starch obtainable by a process as described above. The present phosphate ester of starch has an excellent ink
20 receptivity and very low mottling tendency. Further, it has a high binding power and excellent water and starch retention. In addition it has been found, that the phosphate ester can be used to provide a very stable coating for paper, which provides additional strength to the paper. Also, formaldehyde
25 resins in combination with phosphate esters obtainable in a process according to the invention provide excellent water resistance of paper in the manufacture of which the phosphate esters are employed. In addition, the negative charge of the present phosphate ester of starch is of advantage in
30 retaining starch in the wet end of a paper manufacturing process.

Preferably, the degree of substitution, expressed in moles of phosphorus per mole of starch, and measured colorometrically using molybdate, of a phosphate ester of
35 starch according to the invention lies between 0.005 and 0.5, more preferably between 0.01 and 0.03.

A phosphate ester of starch according to the invention is highly suitable for use in paper, adhesive, food, textile, glass woven, building and oil well drilling applications. Said phosphate ester is particularly useful in the paper industry. Although it may be used in the wet-end, in surface sizing and in coatings, it is in the latter application where its favorable properties have the greatest effect. The main purpose of coating paper is to improve its printability. The most important components of a coating (also referred to as coating color) are pigments, such as titanium oxide, calcium carbonate, clays, and the like, binders, such as latices, starches, PVOH, proteins, and the like, and water. It has surprisingly been found that the advantageous properties of the present phosphate ester, when used as a binder in a paper coating, allow a higher loading of pigment in the paper coating. This results in a more voluminous coating having an increased rigidity, as well as in a reduction in price of the coating.

Another application wherein the present phosphate ester of starch has been found to be highly suitable is in adhesive applications. The product may be used to adhere two or more layers of paper together to form a multi-layer paper or (card)board. In addition, paper and tape may be gummed together with the present product to produce stamps, envelopes, or gummed tape. Further, the present starch ester may be applied as a soluble component in adhesion compositions.

The invention will now be elucidated by the following, non-restrictive examples. Where in these examples reference is made to amylopectin potato starch, a potato starch is meant, which has an amylose content of less than 0.1 wt.%, based on dry substance of starch, as determined using the iodine test.

Example 1 - Preparation of a phosphate ester based on amylopectin potato starch with 5 % urea.

A solution of 40 g urea and 50.8 g phosphoric acid (85 %) in 160 ml of water was adjusted to pH 2.4 with 50 % NaOH. This solution was mixed with 800 g of amylopectin potato starch (moisture 20 %) for 30 minutes in a Hobart mixer. The mixture was equilibrated and subsequently dried in a Retsch fluid bed dryer at 60°C for 30 minutes and at 90°C for 30 minutes. The mixture was heated at 122°C in a fluid bed reactor for 60 minutes. The product was neutralized with solid sodium carbonate to pH 6.

Comparative Example 2 - Preparation of a phosphate ester based on regular potato starch with 5 % urea.

A solution of 40 g urea and 50.8 g phosphoric acid (85 %) in 160 ml of water was adjusted to pH 2.4 with 50 % NaOH. This solution was mixed with 800 g of amylopectin potato starch (moisture 20 %) for 30 minutes in a Hobart mixer. The mixture was equilibrated and subsequently dried in a Retsch fluid bed dryer at 60°C for 30 minutes and at 90°C for 30 minutes. The mixture was heated at 122°C in a fluid bed reactor for 60 minutes. The product was neutralized with solid sodium carbonate to pH 6.

Example 3

The products prepared in examples 1 and 2, and a commercial product were compared in relation to their viscosity in 25 % solution at 50°C. The viscosity was measured using a Brookfield LV viscosity apparatus. The results are shown in Table 1.

Table 1

Starch	Urea (%)	Viscosity (mPas)	Viscosity stability
Nylgum A85	15	195	good
Ex. 1	5	265	good

Comp. Ex. 2 5 > 10000 bad

Commercially available from Avebe, The Netherlands

It was observed that the product of example 1 was of significant lighter colour than the other two investigated products based on regular potato starch.

Example 4 - Preparation of two phosphate esters based on amylopectin and regular potato starch with 2.5 and 1 % urea.

Two other types of phosphate esters were prepared with 2.5 and 1 % urea following the procedure of example 2. In this procedure, the pH of phosphoric acid solution was increased to pH 6.0. Both regular and amylopectin potato starch were used. The results of the products are shown in the following Table 2. The viscosity was measured in 5 % concentration at 50 and 20°C.

Table 2

Starch	Urea (%)	fluid bed temperature	Viscosity 50°C, at t = 0 hrs	Viscosity 50°C, at t = 24 hrs	Viscosity 20°C, at t = 0 hrs	Viscosity 20°C, at t = 24 hrs
amylopectin	2.5	130 °C	1900	2900	3100	4200
amylopectin	1	140 °C	1350	850	2000	1900
regular	2.5	140 °C	1550	>100000	>100000	>100000
regular	1	140 °C	1830	5600	>100000	>100000

From Table 2, it can be concluded that, when using amylopectin potato starch for preparing a phosphate ester of starch, the amount of urea used can be significantly reduced, while still obtaining good product properties.

Claims

1. A process for preparing a phosphate ester of starch, wherein a starch comprising at least 95 wt.%, based on dry substance of the starch, of amylopectin, or a derivative of said starch, is reacted with phosphoric acid or an
5 orthophosphate salt at a temperature of 75-250°C under semi-dry conditions.
2. A process according to claim 1, wherein the starch is a root or tuber starch.
3. A process according to claim 2, wherein the starch is
10 potato starch or tapioca starch.
4. A process according to any of the preceding claims, wherein the starch comprises at least 98 wt.%, based on dry substance of the starch, of amylopectin.
5. A process according to any of the preceding claims,
15 wherein the derivative of starch is obtained by etherification.
6. A process according to any of the preceding claims, wherein the starch is reacted with 0.5 to 10 wt.%, based on dry substance of starch, of phosphoric acid or an
20 orthophosphate salt.
7. A process according to any of the preceding claims, wherein an amount of 0 to 15 wt.%, based on dry substance of starch, of urea is present.
8. A phosphate ester of starch obtainable by a process
25 according to any of the preceding claims.
9. A phosphate ester according to claim 8, having a degree of substitution of 0.005 to 0.5.
10. The use of a phosphate ester according to claim 8 or 9 in the paper industry.
- 30 11. The use of a phosphate ester according to claim 8 or 9 as a binder in a coating for paper.
12. The use of a phosphate ester according to claim 8 or 9 as an adhesive.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08B35/02 C08B31/06 D21H21/00 D21H19/54 C09J103/16

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IPC 6 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 14 43 509 A (BLATTMANN & CO) 9 January 1969 (1969-01-09) page 3, line 6 - line 9 page 3, line 21 - page 4, line 3 page 6, line 6 - line 10 page 8; example 4	1-4, 6-8, 10-12
X	CHEMICAL ABSTRACTS, vol. 91, no. 24, 10 December 1979 (1979-12-10) Columbus, Ohio, US; abstract no. 194924, "Selection of optimum conditions for the phosphating of corn starch amylopectin" XP002114630 abstract & ZUSHMAN A. I. ET AL.: SAKH. PROM-ST, vol. 9, 1979, pages 51-54, -/-	1, 4, 6-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 546 576 A (NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CORPORATION) 16 June 1993 (1993-06-16)	
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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